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Method and device for injecting two-phase CO_2 into a transferring gaseous medium.

The invention relates to a method and device for injecting two-phase "gas+solid" CO_2 into a transferring gaseous medium.

CO_2 is used in many industrial applications: carbonization, pH regulation and neutralization of basic agents are, among others, examples of this. Carbon dioxide may be injected into a liquid medium or a gaseous medium.

CO_2 is injected into a liquid medium in gaseous or liquid form as the case may be.

When carbon dioxide is injected into a gaseous medium, the usual solution is to inject it in a gaseous single phase form. Most often delivered in liquefied form and stored in this form in a tank, at a pressure of the order of 14 to 20 bar and a temperature of the order of -35 to -20°C, it is then necessary to vaporize it. This vaporization requires the on-site presence of a vaporizer which involves a high cost, both operationally as well as in investment, whether the energy is of electrical origin or is provided by steam available on-site. Moreover, the gaseous carbon dioxide feed line as well as the associated accessories (gate valves, valves etc.) are bulky and costly. Thus conventional devices for injecting carbon dioxide into a gaseous medium are not optimized and these devices are in particular not suitable in the case of the injection of large quantities of CO_2.

The use of CO_2 in solid form or as carbon dioxide snow is moreover known for cleaning surfaces.

US 4,747,421 describes the use of solid CO_2 in the industrial field of semiconductors for removing a photoresist film on the surface of a substrate.

EP 0 631 846 describes an apparatus designed to produce an aerosol for cleaning the inner surfaces of a tool room.

EP 0 288 263 describes an apparatus for removing small particles on the surface of a substrate using a mixture of solid and gaseous carbon dioxide.

US 4,389,820 describes a machine designed to generate a stream of accelerated sublimable particles for surface descaling. The use of CO_2 prevents contamination of surfaces as well as atmospheric pollution.

In addition, FR 2 198 778 describes a method and an apparatus for preparing foundry molds, a method in which gaseous carbon dioxide is used for delivering gaseous components in catalytic quantities, both when the mixture of liquid chemical components is gasified as well as when the quantities of components to be added are adjusted.

However, none of the documents cited relates to the enrichment of a transferring gaseous medium with CO_2.

An object of the present invention is to provide a solution to the problem of injecting carbon dioxide, particularly in a large quantity, into chambers containing a reactive or unreactive pressurized transferring gaseous medium.

Another object is to provide an injection device capable of implementing this method.

The features and advantages of the invention will become apparent on reading the following description.

The invention relates first of all to a method for injecting carbon dioxide into a pressurized transferring gaseous medium to be treated, present inside a chamber, from liquid carbon dioxide, the method comprising the following steps:

- converting liquid carbon dioxide into two-phase "gas + solid" carbon dioxide by means of a direct expansion device;

- injecting the two-phase carbon dioxide so formed into the gaseous medium to be treated with the aid of an injector tapped into the wall of the chamber

containing said pressurized transferring gaseous medium to be treated; and

- a step of injecting an inerting gas into the carbon dioxide between the direct expansion device and the injector.

Carbon dioxide is injected in the "gas + solid" form, and injection is carried out directly into the gaseous medium to be treated through a wall of the chamber that encloses the medium to be treated. The chamber may be for example a line or pipeline present in a circuit. Conversion of liquid carbon dioxide into two-phase carbon dioxide makes use of a direct expansion device called a cryogenic expansion device. The device, of the variable-flow valve type, first of all causes the fluid flow to be restricted and then an increase in the flow diameter has the effect of expanding the gas, bringing about a pressure loss so that the pressure at the outlet from the device corresponds to that of the triple point of CO_2. Liquid CO_2 is converted into a mixture of gaseous CO_2 and solid CO_2 (carbon dioxide snow). Thus, during injection, the method of the invention employs a cryogenic fluid with a density at least twenty times greater than its gas phase. Injection of carbon dioxide is carried out using an injector that is tapped into the wall of the chamber and transfers the "gas+solid" mixture to the centre of the pipeline transferring the gaseous medium. Moreover, injection of an inerting gas into the carbon dioxide, at the outlet from the cryogenic valve, prevents blockages in the gaseous medium at the outlet from said valve and at the outlet from the injector. The inerting gas, by ensuring that gas is swept through in the region of the various elements of the device where two-phase CO_2 circulates, prevents contamination by foreign bodies, in particular moisture, and prevents the accumulation of carbon dioxide snow at points where the geometry would make its circulation difficult without entrainment by the inerting gas.

Liquid CO_2 is provided at a pressure generally between 10×10^5 and 22×10^5 Pa (that is between 10 and 22 bar) and at a temperature generally between -35°C and -20°C.

According to a particular embodiment, the two-phase carbon dioxide is injected so that it is injected into the core of the gaseous medium and distributed partly cocurrently and partly countercurrently to the gas stream. By injecting carbon dioxide in this way into the core of the gas, that is to say into the gas current away from the walls, better mixing and entrainment of CO_2 is ensured, in this way preventing it accumulating. Now, the risk of formation of blockages is very great taking into account the temperature of the CO_2 (-80°C). It is therefore essential to disperse this immediately into the gaseous medium to be treated. Apart from the geometry of the injector, the presence of the inerting gas, injected into two-phase CO_2 according to the invention, also makes it possible to limit the risk of blockages.

This inerting gas must be inert to chemical species present as well as to regulating devices (flow-regulating valves, the injector specific to the invention, etc.) It is particularly advantageous to use, as the inerting gas, carbon dioxide coming from the vaporization of a fraction of the available liquid carbon dioxide, and drawn off upstream of the cryogenic expansion device. It will be noted that since CO_2 does not introduce a new chemical species, it can by extension be also considered as an inert gas.

The quantity of carbon dioxide injected is preferably regulated in relation to a set value of a physical or chemical parameter to be attained, measurement of this parameter being carried out in the gaseous medium, downstream from the injection point. Thus, the variable-flow cryogenic valve of the invention is controlled in relation to this set value.

In addition, a safety cryogenic valve of the on/off type can also be placed upstream of the

variable-flow cryogenic valve in order to cut off the feed of liquid CO_2 in the case of malfunction, for example if the pressure is too high in the gaseous medium to be treated, if the temperature is too low there or if another parameter, considered as a major parameter, has exceeded an alarm threshold. The operator of the installation can also control this valve. When the feed to the variable-flow cryogenic valve is cut off, sensitive elements of the device are protected by maintaining a slight flow of inerting gas.

According to another feature, the invention relates to a method for enriching a gas stream with carbon dioxide from liquid carbon dioxide.

According to a particular embodiment, it comprises the following steps :

- converting liquid carbon dioxide into two-phase "gas + solid" carbon dioxide by means of a direct expansion device;
- injecting the two-phase carbon dioxide so formed into the gas stream to be enriched with the aid of an injector tapped into the wall of the chamber containing said gas stream to be enriched;

and in that it includes a step of injecting an inerting gas into the carbon dioxide between the direct expansion device and the injector.

The invention also relates to a carbon dioxide injection device for implementing one of the previously defined methods, characterized in that it comprises:

- a variable-flow expansion valve (designed to be fed with liquid carbon dioxide) and a corresponding injector tapped into a wall of the chamber and penetrating into the core of the gaseous medium;
- a T-piece connected in the upper part to the ejector of the expansion valve (the expansion valve is understood to be the variable-flow valve), connected on the side to a gas feed and connected in the lower part to the injector tapped into said wall;
- means for feeding the expansion valve with liquid CO_2; and

- means for feeding the T-piece with inerting gas.

The end of the injector judiciously consists of:

- a deflector with two slopes distributing the two-phase CO_2 partly countercurrently and partly cocurrently to the gas stream;
- two exhaust openings for ejecting the two-phase CO_2, arranged so as to distribute it in the axis of transfer of the gas stream.

Preferably, the injector enters the chamber over a length equivalent to half the width of said chamber and, according to a preferred variant, the device includes, for feeding the injection device with inerting gas, upstream of the cryogenic expansion device, means for drawing off and vaporizing a fraction of the available liquid carbon dioxide. The device can therefore operate while being connected to a single carbon dioxide feed source. It will also be possible to use an inert gas present on the application site or compressed air, it being understood that the inerting gas should not modify the behavior of the mixture obtained, and should not be counter-indicated for the equipment.

One method for implementing the invention is given by way of a non-limiting example, illustrated by figure 1 which is a diagrammatic view of a device according to the invention and by figures 2 and 2A which represent an example of an injector according to the invention, figure 2A being a sectional view along the axis AA of the end of the injector of Figure 2.

The injection device 1 is designed to provide "gas + liquid" two-phase carbon dioxide into a gaseous medium 2, in transfer under pressure into a chamber 3, and this from a liquid carbon dioxide storage tank 4 in which liquid carbon dioxide is stored at a pressure of between 14×10^6 and 20×10^6 Pa (that is between 14 and 20 bar) and at a temperature of between -35°C and -20°C.

The device 1 comprises a liquid CO_2 feed line formed of a liquid line 5 extending from the tank 4 to

a variable-flow cryogenic valve 6 which provides regulation of a parameter "A" measured in the gaseous medium 2 downstream from the injection point. A filter 7 fitted with a filter cartridge made of stainless steel is placed upstream of the valve 6 and provides filtration of liquid carbon dioxide so as to protect the valve seat from solid impurities that can be present in the pipelines. Interposed on line 5, upstream of the filter 7, there is located a cryogenic safety valve of the on/off type which cuts off the cryogenic CO_2 feed of the valve 6 when the control device 9 detects that the threshold is exceeded for a safety parameter under control. An expansion cryogenic valve, not shown in the figure, protects the line downstream from the safety valve 8 after the latter has been closed.

The device 1 additionally includes a line for feeding inerting gas, which in this case is gaseous CO_2. The line consists, in order, of a vaporizer 10, an expansion device 11, a valve with a manually regulated flow 12, a flow meter with transmitter 13 and a non-return valve 14.

A T-piece 15, supplied at the upper part with two-phase CO_2 coming from the ejector situated at the outlet from the valve 6, and on the side with inerting gas (gaseous CO_2), is connected at the lower part to an injector 16 ensuring injection of the two-phase CO_2 mixture into the pressurized transferring gaseous medium 2 in the chamber 3.

The injector 16 transfers CO_2 to the centre of the pipeline transferring the gaseous medium. When there is no injection of CO_2, the interior of the T-piece 15 and the injector 16 are protected from the medium to be treated by means of a small but continuous flow of inerting gas.

A unit for controlling-regulating the parameter "A" measures the value of the parameter "A" in the transfer pipeline, processes (via the control device 9) the signal received from "A" as well as the signals

coming from different safety parameters followed (temperature and pressure of the gaseous medium to be treated, etc.). It controls, as a function of "A", the amount that the variable-flow cryogenic valve 6 is opened so as to maintain the parameter "A" at its set value. It also controls the closing of the safety cryogenic valve 8 in the case of a major failure affecting a safety parameter, or in the case of a refusal of authorization for treatment on the part of the operator as well as the opening or closing of the vent valve according to the operational mode, generally synchronous with other valves. This control of the control unit is carried out from information communicated by AIT measuring transmitters (measurement of the "A" parameter), PIT measuring transmitters (measurement of the pressure in the gaseous medium 2) and TT measuring transmitters (measurement of the temperature of the medium 2) not referenced. Other elements that are not described can be incorporated in this control unit, in particular binary information of the authorization type or other parameters specific to the method.

Figure 2 represents, in a more detailed manner, an example of an injector according to the invention.

The injector 16 is fed with two-phase CO_2 coming from the ejector 17 at the outlet from the valve 6 and with inerting gas consisting of gaseous CO_2. This feed is carried out via the T-piece 15 that receives the inerting CO_2 at the level of the side inlet 18 and two-phase CO_2 coming from 17 at the upper part. The injector 16, made of a thermally-insulating material, for example polysulfone, leads the "gas + solid" mixture to the centre of the pipeline 3 transferring the gaseous medium 2.

The injector 16 is provided:

- at its end with a deflector 19 with two slopes forming an angle of 80° so as to direct part of the two-phase CO_2 countercurrently to the circulating gaseous medium 2, and the other part cocurrently;

- at its lower part two exhaust openings 20 which are for ejecting two-phase CO_2, even at a low flow rate, and for distributing it in the transfer axis of the gaseous medium, without obstructing the outlet thereof by virtue of their arrangement in the transfer axis.

EXAMPLE

The method of the invention is implemented for enriching vapors from the combustion of natural gas in CO_2. The parameter "A" to be regulated is the CO_2 content of these vapors. Initially at approximately 8% CO_2, the vapors are enriched by the method of the invention to contents of between 12 and 18%, for their subsequent use in a method for producing paper. The vapor flow rate is of the order of 12 000 m^3/h. The quantity of CO_2 used is approximately 1200 m^3/h CO_2 (gas equivalent) to reach 16% CO_2 in the vapors. The vapors enriched in this way are in particular intended for the production of calcium carbonate.

The presence of water vapor in these vapors creates, by reason of the interface between the hot vapors and the cryogenic source, problems associated with the risk of ice formation, particularly in the region of the injector openings. This risk is eliminated by means of permanent inerting of the injector with an inert dry gas.

The method of the invention is in particular applicable in many fields making use of CO_2 as a raw material. Since the enrichment employed according to the invention does not make use of gaseous CO_2, it is free from dimensioning constraints and the disadvantages associated therewith.

The invention is therefore particularly suited to industrial installations having vapors containing CO_2, in itself a polluting agent, and moreover using CO_2 as a raw material.

The method of the invention can also be used in cases where it is desired to treat a transferring gaseous medium with CO_2.

It is also capable of regulating pH using vapors doped with CO_2.

The method of the invention can therefore be applied advantageously to the enrichment of vapors with CO_2 for producing calcium carbonate for industrial papermaking.